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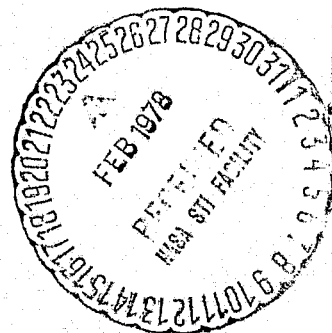
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**MECHANICAL AND PHYSICAL PROPERTIES
OF MODERN BORON FIBERS**

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MECHANICAL AND PHYSICAL PROPERTIES OF MODERN BORON FIBERS

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Introduction

The increased employment of the boron fiber in both low and high temperature composite applications has necessitated a design need for more accurate data regarding its mechanical and physical behavior as a function of temperature. In the past the acquisition of these data was complicated in part by variability in fiber production techniques and in part by the fact that the boron fiber can develop a significant amount of creep strain which is strongly temperature dependent. Recently, however, with the advent of deposition techniques that can produce fibers with relatively consistent tensile strengths, the modern boron fiber has displayed a reproducible microstructure which has allowed experimental and theoretical studies of its deformation strain as a function of environmental parameters (1) (hereafter referred to as paper I). The primary objective here is to complete the mechanical property study described in paper I by reporting the results of accurate measurements of the modern boron fiber's Young's modulus, flexural modulus, shear modulus, and Poisson's ratio. Physical property data concerning fiber density, thermal expansion, and resistance obtained during the course of the mechanical studies will also be reported.

The boron fiber specimens employed for the property measurements were commercially supplied by Avco Systems Division with average tensile strengths above 3 GN/m^2 and nominal diameters of $102 \text{ }\mu\text{m}$ (4 mil), $142 \text{ }\mu\text{m}$ (5.6 mil), $203 \text{ }\mu\text{m}$ (8 mil), and $375 \text{ }\mu\text{m}$ (15 mil). These fibers were chemically vapor deposited in a single stage reactor by the hydrogen reduction of boron trichloride on a resistively heated wire substrate which continuously passed through the reactor. In order to minimize production time and achieve consistent strength properties the temperature profile of the fiber-substrate was maintained near 1300°C . For the two larger diameter fibers this required the addition of induction heating coils near the exit end of the reactor. For the majority of the specimens the substrate was $13 \text{ }\mu\text{m}$ (0.5 mil) tungsten wire which became completely borided to form a $17\text{-}\mu\text{m}$ (0.67 mil) diameter core after deposition. The remaining fibers were formed on a substrate consisting of a $34\text{-}\mu\text{m}$ (1.3-mil) carbon monofilament coated with a $3\text{-}\mu\text{m}$ (0.1-mil) layer of pyrolytic graphite. Whereas the tungsten substrate was available for all four diameters, the carbon substrate was available only in the 102 and $142 \text{ }\mu\text{m}$ fiber sizes.

Procedure

Background

The deformation of a boron fiber has been observed to be characteristically anelastic (1,2,3). That is, in a creep test upon application of a constant tensile stress σ at time $t = 0$, the total strain ϵ^D in the fiber increases with time t and temperature T according to

$$\epsilon^D(t, T, \sigma) = \epsilon^e(T) + \epsilon^a(t, T, \sigma) \quad (1)$$

Here $\epsilon^e = \sigma/E^e(T)$ is the time-independent elastic strain which depends on T only through the elastic Young's modulus E^e . The anelastic creep strain ϵ^a is zero at $t = 0$ but increases with time, temperature, and stress. Three properties which characterize ϵ^a and distinguish it from plastic strain are:

- I. Linearity: ϵ^a is directly proportional to σ .
- II. Equilibrium: After passage of sufficient time, ϵ^a reaches or relaxes to a unique equilibrium value.
- III. Recoverability: Upon removal of σ , the developed ϵ^a completely disappears at a rate which is time and temperature dependent.

Because of property I it is convenient to introduce a stress-independent anelastic strain ratio A defined by

$$A(t, T) = \left(\frac{\epsilon^D}{\epsilon^e} \right) (t, T) = \frac{E^e(T)}{\sigma} \epsilon^D(t, T, \sigma) \quad (2)$$

Also from property I, if a constant strain ϵ is applied at $t = 0$, the resulting stress $\sigma(t, T, \epsilon)$ will be linear with ϵ , so that for a stress relaxation test one can introduce a strain-independent anelastic stress ratio m where

$$m(t, T) = \frac{\sigma(t, T, \epsilon)}{\sigma(0, T, \epsilon)} = \frac{\sigma(t, T, \epsilon)}{\epsilon E^e(T)} \quad (3)$$

For boron fibers the microstructural processes responsible for ϵ^a relax over a broad temperature range (1) so that

$$m(t, T) = [A(t, T)]^{-1} \quad (4)$$

Therefore, to predict boron fiber creep $\epsilon^D(t, T, \sigma)$ or stress relaxation $\sigma(t, T, \epsilon)$ one must determine $A(t, T)$ and $E^e(T)$.

Although the above discussion was based on the application of a uniform axial stress, the anelastic property I implies that if the stress distribution in the fiber is not uniform, the elastic and anelastic strain components in each volume element will be directly proportional to the stress in that element. Thus, as long as the linearity property holds, the stress-independent A ratio will be the same in each volume element and therefore independent of the applied stress distribution. For this reason, both axial and flexural strain measurements should yield the same $A(t, T)$ by Eq. (2). For the flexural studies, ϵ^D and σ can be conveniently taken as the maximum surface strain ϵ_s and stress σ_s , respectively.

Mechanical Properties

The strain ratio $A(t,T)$ for modern boron fibers was determined in paper I primarily from flexural measurements. The approach was simply to measure as a function of temperature the amount of flexural stress relaxation after a certain time. With the aid of anelasticity theory long time data of 1 hour were then best fitted with short time data of $\sim 10^{-3}$ second to calculate an $A(t,T)$ for all times, temperatures, and stresses within the ranges examined. The long time flexural stress relaxation (FSR) data were taken on both cantilevered and constant bend radius specimens, whereas the short time data were obtained from flexural internal friction (FIF) measurements on cantilevered specimens in the frequency range 10^2 to 10^4 hertz. From the FSR results it became clear that A was not independent of stress if surface strain exceeded 10^{-3} . To study this effect stress rupture measurements were made as a function of temperature on specially etched 203 μm fibers. Details of the FSR, FIF, and stress rupture experiments and data analysis are described in paper I.

In this work emphasis was placed on obtaining accurate room temperature data for the fiber elastic Young's modulus E_Y^e , flexural modulus E_b^e , and shear modulus G^e . These measurements were somewhat complicated by the fact that for any finite time and stress at 295 K there existed some anelastic contribution to the fiber strain. Thus, for example, a measurement of Young's modulus would be Eq. (2) be both time and temperature dependent; i.e.,

$$E_Y(t,T) = \frac{\sigma}{\epsilon^D(t,T,\sigma)} = \frac{E_Y^e(T)}{A(t,T)} \quad (5)$$

In order to obtain the desired elastic modulus, it was necessary, therefore, to correct any modulus measurement by the $A(t,T)$ appropriate to the test method.

For the E_Y measurements two different procedures were employed. The first method consisted of optically measuring fiber elongation while holding stress constant at both 77 and 295 K. The A corrections for anelastic strain in the elongation data are discussed with the results. The second method for obtaining E_Y consisted of measuring free-free flexural resonant frequencies for various 50 volume percent unidirectional boron/aluminum composite bars. Details of the experimental procedure and data analysis are described elsewhere (4). The average room temperature anelastic correction for the dynamic composite data as well as all other fiber vibration data ($10^2 - 10^4$ Hz) was determined to be $A = 1.01$.

For determination of flexural modulus E_b , cantilevered fibers were vibrated at fundamental resonance at low strain amplitude in air. The frequency f_b of the resonant mode is related to E_b by

$$f_b = 0.1399 \frac{d}{l^2} \left(\frac{E_b}{\rho} \right)^{1/2} \quad (6)$$

where d , l , and ρ are the specimen diameter, length, and density (including core), respectively. For determination of shear modulus G , two small tantalum or stainless steel plates ($10 \times 2 \times 0.3$ mm) were spot-welded together around the lower end of a vertical fiber to form an inverted T-shaped configuration. When the upper fiber end was clamped in a pin vise, the

mechanical gripping force of the plates was enough to allow the entire specimen to be vibrated in air as a torsion pendulum. The resonant frequency f_G of the plate-fiber configuration is related to the fiber G by

$$f_G = \frac{d^2}{8} \left(\frac{G}{2\pi I l} \right)^{1/2} \quad (7)$$

where I is the moment of inertia of the plates around the fiber axis. The electrostatic drive and pickup systems for both the flexural and torsional vibrations were the same as those employed in the FIF studies.

Clearly, to achieve accurate data for the elastic moduli it was necessary to make accurate measurements of specimen dimensions and density and then to correct the calculated moduli for air damping and internal anelasticity. Diameter data were taken directly with a calibrated split-image microscope and indirectly by measurements of mass per length and density of the vibrated specimens. The optical diameter measured from the fiber shadow image was slightly larger ($\sim 0.7 \mu\text{m}$) than the diameter calculated by mass measurement. This difference which appeared to be independent of as-received fiber size was interpreted as the difference in the maximum fiber diameter and the effective diameter which averages the roughness of the characteristic "kernel" surface. Because of its averaging character the mass measurement of effective diameter was employed in all modulus calculations. Since flexural length to diameter ratios were kept above 100, no correction to the constant in Eq. (6) was introduced for Timoshenko shear effects (5). However, because flexural vibration nodes occurred slightly within the clamp of the cantilevered specimens, measured fiber lengths had to be corrected by the addition of a small increment ($\sim 0.1 \text{ mm}$). This correction was made by taking a series of f_b versus l data for each specimen and then finding the slope of the least squares fit line for a plot of l versus $(f_b)^{1/2}$. By Eq. (6) this slope is proportional to $(E_b)^{1/4}$. A similar procedure was used for the G measurement to account for length corrections due to the finite width of the added plates and possible torsional motion within the pin vise. Finally, by observing the increase in f_b by removal of air, it was determined that the average air damping correction was $\Delta E/E = +0.2$ percent. This small value was also applied to the G data.

Physical Properties

Density. - For the purpose of understanding the microstructure of modern boron fibers and calculating their flexural modulus, a liquid density gradient column was prepared according to ASTM test D 1505 (Method C). Final density distribution ranged from 2.25 to 2.50 g/cm^3 with a gradient of 0.0003 g/cm^3 per mm of column height. Linearity was excellent as evidenced by five evenly spaced calibration floats accurate to 0.0001 g/cm^3 . Before each measurement the ends of the fiber were mechanically squared as much as possible in order to avoid density errors caused by overexposure or underexposure of the highly dense core region. However, for the fiber lengths employed (2 to 3 cm), it was estimated that unprepared fiber ends would at worst produce a density error of only 0.0005 g/cm^3 (as measured at the fiber's center of gravity).

Thermal Expansion and Resistance. - In the course of an experimental program to resistance heat 203 μm boron fibers in argon (6), it was necessary to construct an apparatus similar to a commercial deposition reactor. This apparatus was employed to measure both fiber thermal expansion and resistance. The heated fiber length could be varied in order to determine any contributions from the mercury-containing electrodes. The fiber was kept rigid in the tube by a fixed clamp above the top electrode and a hanging clamp (9 grams) below the lower electrode. The flow rate of nominally pure argon was varied

Employing this definition of q and Eqs. (3) and (4), one can convert either the low strain FSR or FIF data to the $A_L(q)$ plotted in Fig. 1. The subscript L (low) is used to denote that A_L applies only at stresses below $\sim 1.0 \text{ GN/m}^2$. Data points for A_L are not indicated because of their almost continuous nature and negligible error.

Although A_L was indeed observed to be stress independent below 1.0 GN/m^2 , FSR measurements on fibers held at constant bend radius indicated that A for surface strains near 6×10^{-3} was measurably greater than A_L in the time-temperature range $10 < q < 30$. Although this increase in A might at first be interpreted as evidence of stress-induced plasticity, it was observed that all strains developed in the high stress measurements could be completely removed by thermal treatment. Because this is the anelastic property of complete recoverability, the onset of a stress-dependent A ratio was interpreted rather as a stress-induced increase in the number of microstructural mechanisms giving rise to boron fiber anelastic strain. As such, above 1.0 GN/m^2 the A would be expected to increase and then saturate when all anelastic mechanisms are fully activated. Thus it became necessary to determine (a) the stress level at which A saturates and (b) the absolute value for $A_H(q)$, the anelastic strain ratio at high (H) stress.

The approach taken in paper I to determine A_H was based on the 295 K ultimate tensile strength (UTS) results of Smith (10). He found that after etching a few micrometers off the surface of as-received 203 μm fibers, essentially all cases of fracture could be explained by crack initiation within the region of the tungsten boride core. This result suggests a fracture model in which an etched 203 μm fiber fractures whenever its total axial strain $\epsilon^D(t, T, \sigma)$ become equal to the core fracture strain. By assuming a brittle elastic core with a fracture strain essentially independent of temperature, our approach to determining A_H was simply to measure the fiber fracture stress $\sigma_F(t, T)$ required for the anelastic boron sheath to attain the fiber fracture strain observed at 295 K. Neglecting stress contributions of the core and assuming the fracture stresses were well above the level to saturate A , one can then calculate $A_H(q)$ from Eq. (2):

$$A_H(q) = \left[\frac{E_Y^e(T)}{E_Y^e(295 \text{ K})} \right] \left[\frac{\sigma_F(q_0, d_1)}{\tau_F(q, d_1)} \right] A_H(q_0) \quad (9)$$

where d_1 is the diameter of the etched fiber and q_0 is the time-temperature parameter for a fracture test at 295 K.

For the above work 203 μm fibers were etched down to $d_1 = 143 \mu\text{m}$ so that from Smith's results $\sigma_F(q_0, d_1) = 5.03 \pm 0.16 \text{ GN/m}^2$. Here $q_0 = 11.6 \text{ K}$ because for a tensile test with monotonically increasing stress, the time t can be taken as the time interval between initial stress application and fracture (1). The methods used for evaluating the Eq. (9) modulus ratio and $A_H(q_0)$ are explained with the elastic moduli results. To obtain $\sigma_F(q, d_1)$ the etched fibers were subjected to UTS measurements at 77 K and to high temperature stress rupture measurements. The A_H calculations from these fracture stress data are shown as the closed circles in Fig. 1. The modulus measurement of $A_H(q_0)$ is shown by the open rectangle. Because of this last result the A_H values of Fig. 1 are slightly lower (0.08) than those reported in paper I.

In the microstructural model of boron fiber anelasticity it is assumed that as stress rises above zero, A remains constant and equal to A_L . As some particular stress level A rises above A_L until some higher stress

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level is reached where A becomes stress-independent again and equal to A_H . Although the A_H data are less accurate than the A_L data, the Fig. 1 results for $q > 10$ do support such a model. It should be made clear that the stress rupture data used to calculate A_H decreased from 5 to 3 GN/m² and therefore by themselves could not establish the stress independence of the results. However, from paper I in which room temperature axial creep data (11) were examined according to anelasticity theory, it does appear that the A_H of Fig. 1 can be observed as low as 1.5 GN/m². The stress independence of A_H is also supported by the stress rupture results of Veltri and Galasso (12). Their data when averaged and converted to A ratios by Eq. (9) yield the open circles of Fig. 1. It can be seen that although the stresses of this latter study were measurably lower, decreasing from 3 to 2 GN/m², the calculated A values are in good agreement with the solid A_H curve. Thus it appears that the change in A ratio occurs over the relatively narrow range between approximately 1.0 and 1.5 GN/m². Also plotted in Fig. 1 are the A values corresponding to FSR on constant bend radius fibers. The resulting curve labeled A_b can be interpreted as some combination of A_L and A_H as one might expect for a flexed fiber with an internal stress gradient ranging from zero at the core to ~2.4 GN/m² at the surface.

Summarizing the design implications of Fig. 1, one can treat boron fibers as strictly elastic solids (unity A) only if the time-temperature conditions of the stress application yield a q value below 10. For those situations in which $q > 10$, one can estimate their deformation strain from

$$\epsilon^D(t, T, \sigma) = \frac{\sigma}{E^e(T)} A_\sigma(q) \quad (10)$$

Here ϵ^D is the total tensile (or flexural surface strain), σ is the applied tensile (or flexural surface), stress, E^e is the fiber elastic Young's (or flexural) modulus, q is the time-temperature parameter given by Eq. (8), and A_σ is the anelastic strain ratio appropriate to the stress level. For any type of stress below 1.0 GN/m², A_σ is given accurately by A_L . For stresses above 1.5 GN/m², $A_\sigma \cong A_H$ for tensile conditions, and $A_\sigma \cong A_b$ for flexural conditions. As will be discussed, it can be assumed that for the common fiber sizes under tensile stress, core effects on A_σ can be neglected.

Elastic Moduli

The results of the various methods employed to measure the elastic moduli of boron fibers at room temperature are given in Table I. At least three fibers were used for each measurement. All specimens contained tungsten-boride cores.

Young's Modulus. - Although there existed some scatter, the average E_Y^e (295 K) determined by the 77 K elongation method and the boron/aluminum composite method were in close agreement. For the elongation technique the test conditions were such that A in Eq. (5) could be taken as unity. The 77 K modulus was then divided by 1.006 according to the temperature dependence of E_Y^e (to be discussed below).

Because anelastic strains exist at all stress levels the E_Y^e values given in Table I could not be observed for any normal room temperature elongation measurement. This was verified by performing such tests on the same fibers used for the 77 K data. The 295 K result was $E_Y(q_0) = 390 \pm 8$ GN/m².

Both E_Y^e and $E_Y(q_0)$ were purposely measured above 1.5 GN/m² so that by Eq. (5), $A_H(q_0)$ could be calculated simply from their ratio. The result is indicated by the open rectangle on the A_H curve in Fig. 1.

In order to determine the tungsten-boride core contribution to E_Y^e , the boron sheath was completely removed from 203 μm fibers by electropolishing (13). Density data for free cores suggest a two-phase system, the region within 13 μm being all W_2B_5 and the region between 13 and 17 μm being a mixture of WB_4 and boron. With this model flexural resonance data for cores with various electropolished diameters could be best explained by assigning average moduli of 670 GN/m^2 to the W_2B_5 and 420 GN/m^2 to the outer core region. These findings indicate an axial core modulus of $\sim 550 \text{ GN/m}^2$. Thus, if the fiber core behaves as a free core, it should contribute only about 1 and 2 GN/m^2 to the E_Y of 203 and 102 μm fibers, respectively, and thereby have essentially no effect on fiber axial deformation.

Regarding boron fibers deposited on carbon substrate, the core contributions to Young's modulus are expected to be greater because of the substrate's size and lower modulus. Assuming a boron sheath modulus of 418 GN/m^2 and a 37- μm core modulus of 41 GN/m^2 (14), one calculates an E_Y^e for modern boron on carbon fibers of 369 and 393 GN/m^2 for 102 and 142 μm fiber diameters, respectively. Although this is a much larger modulus effect than that of the tungsten boride core, one might assume to a first approximation that the carbon core affects the Eq. (10) fiber axial deformation only through the modulus term.

Flexural Modulus. - The 295 K flexural modulus results given in Table I show little variation with diameter but a measurable difference from the axial Young's modulus. From the above discussion on the core contributions to E_Y^e it is apparent that there must be a source other than the tungsten-boride core to explain the lower E_b^e values. As will be demonstrated in the density results for etched fibers, the density within the as-received boron sheath increases with decreasing radius, a physical property that might be expected from the nature of the deposition process. Because lower than theoretical densities can lead to lower than theoretical moduli in ceramic materials (15), it is suggested that it is the lower than average surface density of the boron fiber that is the primary source of a flexural modulus which is lower than average sheath modulus of about 418 GN/m^2 .

Shear Modulus. - The elastic shear modulus results of Table I are in excellent agreement with the G value reported in the past for boron fibers (16).

Poisson's Ratio. - If it is assumed that in any volume element in the boron sheath the elastic properties are isotropic, one can calculate Poisson's ratio for that element by $\nu = (E/2G) - 1$. The modulus results for E_b^e and G^e were employed to calculate the fiber ν values given in Table I.

The average Poisson's ratio result of 0.13 is lower than the value 0.20 commonly quoted in the literature. This difference can probably be attributed to the use of the larger E_Y value in prior ν calculations. However, because G and E_b are both determined by volume elements near the fiber surface, we believe that 0.13 is a more accurate value for the Poisson's ratio of the boron sheath and thus of the boron fiber. Support for this value can be found in the model which explains the anelastic effects near $q = 20$ by the "grain-boundary sliding" of boron icosahedra past each other (3). For $\nu = 0.13$ theory predicts that when all mechanisms are operative $A = 1.84 \pm 0.04$, a result which is in good agreement with the maximum observed in A_H near $q = 25$ (Fig. 1).

Temperature Dependence. - The temperature dependence of the moduli was determined from flexural resonant frequencies f_b as a function of temperature (1). By manipulation of Eqs. (5) and (6) one finds

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$$\frac{E_b(T)}{E_b(T_o)} = \left[\frac{f_b(T)}{f_b(T_o)} \right]^2 \left[\frac{A_L(t, T)}{A_L(t, T_o)} \right] \left[\frac{1 + \lambda(T)}{1 + \lambda(T_o)} \right] \quad (11)$$

where $T_o = 295$ K, $t = (2\pi f_b)^{-1}$, and $\lambda(T)$ is the boron thermal expansion strain. The result of inserting f_b data into Eq. (11) is shown in Fig. 2. For design purposes one can assume that the core has negligible effects and that Poisson's ratio is independent of temperature so that the Fig. 2 curve applied for both $E_Y^E(T)$ and $G^E(T)$.

Mechanical Properties

With a fairly accurate knowledge of the elastic moduli and the $A(q)$ one can now design for the time, temperature, and stress dependence of all the significant mechanical properties of modern boron fibers. These properties which are derivable from the deformation strain relation of Eq. (10) include creep strain, creep recovery, stress relaxation, damping capacity, and fracture stress (Eq. (9)). Because the effects of environmental conditions on the above properties have already been discussed in paper I, we will concern ourselves here only with those mechanical properties for which more discussion is considered useful to elucidate practical and basic implications.

Damping Capacity. - The damping capacity ψ of a vibrating system is the ratio of the energy loss per cycle to the total stored energy. Because the energy loss in a vibrating boron fiber is produced by the anelastic strain being out of phase with the alternating applied stress, it follows that (17)

$$\psi_\sigma(f, T) = \frac{\pi^2 T}{10^3} \left[\frac{1}{A_U} \frac{dA_\sigma}{dq} \right]_{t=(2\pi f)^{-1}} \quad (12)$$

where f is the stress frequency. Typical $\psi_L(T)$ results obtained near 500 hertz by low stress flexural internal friction measurements are shown in Fig. 3. Data such as these were employed to make accurate calculations of the $A_L(q)$ curve of Fig. 1. Although high stress $\psi_H(T)$ measurements have yet to be made, one can insert the Fig. 1 A_H into Eq. (12) to obtain the approximate dashed curve in Fig. 3 for frequencies near 500 hertz. Clearly from Eq. (12) the significantly high peaks in the ψ curves occur at the inflection points in the $A(q)$ curves. Lower frequencies (higher q) shift the peaks toward lower temperatures; whereas higher frequencies (lower q) shift the peaks toward higher temperatures.

In previous work the effect of high temperature treatment on the damping characteristics of 203 μ m fibers were measured (3). Comparing the ψ_H curve of Fig. 3 with the ψ result on fibers whose boron sheath was completely converted to crystalline β -rhombohedral boron, one finds very good agreement both in curve height and curve shape (i.e., time-temperature dependence). This observation suggests that the application of stresses above 1.5 GN/m² affects the anelastic mechanisms in the as-deposited amorphous microstructure in such a way that they behave as if they existed in a β -rhombohedral crystalline environment.

Stress Relaxation. - If in a stress relaxation test a constant strain ϵ is maintained, the stress σ within a boron fiber will decrease according to the relation

$$\sigma(t, T, c) = \frac{\sigma(o, T, \epsilon)}{A_{\sigma}(t, T)} = \frac{\epsilon E^c(T)}{A_{\sigma}(t, T)} \quad (13)$$

Because stress is not constant, care must be taken in choosing the appropriate A_{σ} for predicting the q dependence of σ . For example, if the initial σ were less than 1 GN/m^2 , then A_L would apply for all q . However, if the initial σ were greater than 1.5 GN/m^2 , then A_H would apply only until $q = q^*$ where q^* is the value at which the stress relaxes to $\sigma^* \approx 1.5 \text{ GN/m}^2$. For $q > q^*$ there would occur a transition in A from A_H to A_L . From the A results of Fig. 1 one can reason that at high temperature high stresses will relax rapidly to σ^* and then decrease relatively slowly from that point on. It is possibly this type of behavior which accounts for the fact that neither axial tensile nor compressive internal stresses within as-received boron fibers are ever observed to exceed 1.5 GN/m^2 (14).

Creep Formability. - For some recent composite applications there has developed a need to creep bend boron fibers. One method for accomplishing this is that employed in the FSR studies in which a fiber is bent around a cylindrical mandrel of radius of curvature b_o and then heat treated to allow stress relaxation to occur. When the fiber is removed from the mandrel at room temperature, it displays a circular bend of radius of curvature b_1 where $b_1 > b_o$. This b_1 bend is due entirely to anelastic strain and thus can be completely removed by reheating (property of creep recovery).

To determine the proper time-temperature conditions for producing a certain b_1 , one can use the fact that flexural surface strain $\epsilon_s = d/2b$ so that from Eq. (13)

$$\begin{aligned} [A_{\sigma}(q)]^{-1} &= \frac{\sigma_s(t, T, \epsilon_o)}{\sigma_s(o, T, \epsilon_o)} = 1 - \frac{\epsilon_s^a}{\epsilon_o} (t, T) \\ &= 1 - b_o/b_1(q) \end{aligned} \quad (14)$$

If the initial surface stress $E_b d/2b_o$ is less than σ^* , then $A_{\sigma} = A_L$. For the more common case in which small b_1 are desired, b_o must also be small, thereby making the initial stress greater than σ^* . In this case $A_{\sigma} \approx A_b$ is a good approximation since the A_b of Fig. 1 was indeed determined by the high stress circular bend method. It should be pointed out that etched $203 \mu\text{m}$ fibers exhibit flexural surface strains as high as 3 percent before fracturing (10). Subjecting these fibers to a heat treatment of $A_b = 2$, one can obtain very small b_1 radii of $\sim 33 d_1$ where d_1 is the etched diameter. Some fraction of b_1 will recover, however, if after removal from the mandrel the fiber is subjected to time-temperature conditions of $q > 10$. For room temperature this effect is small but for higher temperatures recovery can become significant. A method for determining anelastic creep strain recovery is discussed in paper I.

Physical Properties

Density. - The density results for as-received fibers deposited on both tungsten and carbon substrates are given in Table II. Modeling the fiber as a two-phase composite, one expects the fiber density ρ to vary with sheath diameter d_o according to

$$\rho = \bar{\rho}_B + C/d_o^2 \quad (15)$$

where $C = d_c^2(\bar{\rho}_c - \bar{\rho}_B)$, d_c is the core diameter, and $\bar{\rho}_B$ and $\bar{\rho}_c$ are the average boron sheath and core densities, respectively. If the $\bar{\rho}_c$ for the three fiber sizes with tungsten-boride cores are fitted to Eq. (15), linearity in d_o^{-2} is found when $C(W) = 2596 \pm 13 \mu m^2 \cdot g/cm^3$ and

$$\bar{\rho}_B = 2.3465 \pm 0.0004 \text{ g/cm}^3 \quad (16)$$

Using this sheath density for the one fiber size with carbon core, one finds $C(\text{Carbon}) = -1050 \mu m^2 \cdot g/cm^3$.

The low scatter in $\bar{\rho}_B$ and $C(W)$ coupled with the fact that the different fibers were produced under different deposition conditions suggest that for fiber sizes 142 μm and larger: (a) the tungsten-boride core density contribution is fiber size independent, (b) the density distributions in the as-received fibers are similar, and (c) the value $\bar{\rho}_B = 2.3465 \text{ g/cm}^3$ is probably close to the theoretical density of amorphous boron. To examine these conclusions further, measurements were made of the densities of 203 μm fibers etched to smaller diameters in hot nitric acid (10). The densities and final diameters of the etched fibers are also given in Table II.

To determine density variation in the as-received boron sheath, the average density $\bar{\rho}_{01}$ of each outer layer removed by etching was determined from

$$\bar{\rho}_{01} = \frac{\rho_o d_o^2 - \rho_1 d_1^2 (1 + \epsilon_1)}{d_o^2 - d_1^2 (1 - \nu_1)^{-2}} \quad (17)$$

Here subscripts o and 1 refer to original and etched values, respectively; ϵ_1 (negative) is the fiber axial contraction at d_1 due to residual stress (13); and Poisson's ratio is taken as 0.13. The unknown effects of residual radial stress have been neglected. Plotting $\bar{\rho}_{01}$ versus average radius $(d_o + d_1)/4$, one obtains the Fig. 4 result for radial density variation in the as-received 203 μm boron sheath. The dashed line assumes that density eventually saturates and that the average sheath density is 2.3465 g/cm^3 .

Qualitatively Fig. 4 suggests that each layer of boron is deposited with less than maximum density. As time progresses and outer layers are added, radial atomic diffusion occurs inward tending to reduce voids and increase density in the inner layers. Quantitatively the surface density is less than average but this difference is quite small. Even if axial residual stresses (13) are considered, the difference only doubles. This result as well as the size independence of $\bar{\rho}_B$ thus supports the conclusion that the theoretical amorphous density is equal to about 2.35 g/cm^3 .

If a less than theoretical density implies a less than maximum modulus (15), Fig. 4 would indeed explain the Table I data in which the flexural modulus E_b^e is lower than the Young's modulus E_Y^e . If a given density produces a certain modulus, the low scatter in E_b^e with fiber size supports the earlier conclusion that the density variation of Fig. 4 is size independent. That is, plotting density versus normalized radius should yield similar curves for all the examined fiber sizes. Similar behavior has also been observed for the residual axial stress distribution (13). Pursuing the density-modulus relationship further one can associate $\bar{\rho}_B$ with E_Y^e and in the extreme $\rho(d_o)$ with E_b^e and find that for amorphous boron a small density change of 0.3 percent can produce a large modulus change of ~ 4 percent. This model may explain the fact that boron fibers have been produced with modulus values (corrected for anelasticity) as high as 470 GN/m^2 (18). Perhaps these fibers were deposited at maximum density.

Thermal Expansion. - To determine boron fiber axial strain as a function of temperature, length changes were measured for 203 μm fibers resistance-heated above 1000 K. These measurements which were made with fiber lengths of 16, 32, and 64 cm showed no end effects due to the electrodes. The length change results normalized to expansion strain λ are shown as open circles in Fig. 5.

For thermal expansion at low temperatures, the data of Fig. 5 were best fitted to the Gruneisen equation for thermal expansion coefficient $\alpha(T)$:

$$\left(\frac{C_V}{3\alpha}\right)_T^{1/2} = \left(\frac{C_V}{3\alpha}\right)_{T=0}^{1/2} - 0.01 U(T) \quad (18)$$

Here C_V is the specific heat at constant volume (cal/mole $^{\circ}\text{C}$) and U is the internal energy (cal/mole) (19). Because the Debye temperature of amorphous boron is ~ 1200 K, the approximation $C_V = C_P$ is fairly accurate for $T < 1200$ K. With the amorphous $C_P(T)$ and $U(T)$ results of Wise, et al. (20), we have inserted the α for the high temperature data in Eq. (18) to determine best fit constants. The result in terms of thermal expansion strain

$\lambda = \int \alpha \, dT$ is given by the solid lines of Fig. 5. Since at low temperatures α , the slope of the curve, is constantly varying, it is probably more useful for design purposes to describe boron fiber expansion by the λ strain over a particular temperature interval. Because the tungsten-boride core is small and estimated to expand in a manner similar to boron (1), the Fig. 5 result is expected to be independent of fiber size. The effect of the somewhat larger carbon core on the boron fiber expansion was not determined.

Resistance. - The temperature-dependent resistance of 203 μm boron fibers was measured from the voltage and current required to resistance heat the fibers in argon. End resistances ($\sim 245 \, \Omega$) due primarily to the passage of current from the mercury through the boron sheath to the core were determined at each temperature by employing heated fiber lengths of 16, 32, and 64 cm. Fiber temperatures above 1000 K were measured with an optical pyrometer; whereas temperatures below 1000 K were determined from Fig. 5 and the measured thermal expansion strain. The normalized resistance results with end effects eliminated are given in Fig. 6 in terms of resistance per unit length R .

Because of parallel current paths, the boron fiber resistance R is determined by both the sheath resistance R_B and the core resistance R_C . Due to the semiconducting electrical properties of crystalline boron (21), the R_B of the amorphous sheath is expected to very high at low temperature and then decrease exponentially as temperature increases. On the other hand, due to its metallic nature the core resistance R_C should be relatively low and show a linear temperature dependence. Thus the Fig. 6 curve for R can be explained simply by primary core conduction up to 800 K and primary sheath conduction above 1000 K.

Based on the above fiber electrical model one can now use Fig. 5 to examine the individual resistivity properties of the tungsten-boride core and the boron sheath. For example, by linearly extrapolating the R curve down to 295 K one can determine core resistivity γ_C at room temperature, i.e., $\gamma_C/d_c^2 = 26.9 \, \Omega \cdot \text{cm}$. As previously discussed in the E_V results, the 17 μm core, like the fiber, is a composite in itself consisting of a 13 μm W_2B_5 central region surrounded by an outside annulus of WB_4 and boron. The 295 K resistivity of W_2B_5 has been measured to be 43 $\mu\Omega/\text{cm}$ (22). If the γ of the WB_4 is assumed to be high like the γ_B for boron, it follows from the 295 K result and the γ value for W_2B_5 that d_c for W_2B_5 is 12.6 μm ,

a diameter in excellent agreement with the core density data. Thus it appears that although the core has an optical diameter of 17 μm it is essentially the central 13 μm W_2B_5 region that carries the entire fiber current at low temperature.

For determination of the boron sheath resistivity γ_B , one can linearly extrapolate the R curve upward to estimate the core resistance at high temperature. With the parallel circuit fiber model, one can then use R_c and the measured R to determine sheath resistance and resistivity. Because of the R scatter and errors in the extrapolation of R_c , it was not possible to achieve very accurate γ_B . However, the high temperature results could be fitted to the form

$$\gamma_B = \gamma_B^0 \exp(Q/2kT) \quad (19)$$

as would be expected for a semiconducting sheath. The data averages yielded $\gamma_B^0 = 5.0 \mu\Omega\text{cm}$ and $Q = 1.67 \text{ eV}$. The Q value is close to the thermal band gap energy as determined from the resistivity of β -rhombohedral boron (21).

From the above results it can be assumed that at temperatures below 800 K boron fiber resistance for the common sizes will be determined entirely by the core and thus given by the Fig. 6 results. As for fibers with carbon core, quoted 295 K resistance values of $\sim 450 \Omega/\text{cm}$ for the carbon monofilament (14) indicate that it also should control fiber resistance up to $\sim 800 \text{ K}$.

Concluding Remarks

For advanced composites reinforced by modern boron fibers, the baseline mechanical and physical data presented here and in paper I provide much of the information needed for design situations in which time-temperature dependent fiber properties play a significant role. Although the concept of a modern fiber has been emphasized, it appears from property data comparison with "older" boron fibers that it is only in the area of fracture strain that any great difference can be observed. Thus the prime property change produced by modern deposition techniques has been the elimination of low strength flaws. Whether future changes in deposition procedures are needed is not clear at the present time. The data of Smith implies that for the 203 μm fiber the lowest strength flaws in the bulk boron induce fracture well above 5 GN/m^2 whereas surface and core flaws are the source of the as-received fiber strengths between 3 and 4 GN/m^2 (10). Because this suggests that fiber fracture improvement should center primarily on core and surface alteration, the properties of the bulk boron for any future fiber will probably not differ significantly from those presented here. This being the case, by applying the composite concept to the fiber itself, one should be able to predict any nonfracture fiber property from the volume fractions and constituent properties of the sheath and other components. These other components can include new cores, surface coatings, or even matrix-fiber interaction phases. In most cases, however, the volume fraction of the second component will be small enough that its influence on nonfracture behavior can be neglected.

Nomenclature

A: A_σ, A_L, A_H	Anelastic strain ratio: stress-dependent A, low stress A, high stress A (Eq. (2))
b: b_o, b_l	Bend radius of curvature: initial, final
C: C_v, C_p	Specific heat: at constant volume, at constant pressure
d: d_o, d_l	Fiber diameter: before etching, after etching

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E: E_b, E_y	Tensile modulus: flexural, Young's
f: f_b, f_G	Frequency: for flexural resonance, for torsional resonance
G	Shear modulus
I	Moment of inertia
k	Boltzmann's constant
l	Fiber length
m	Anelastic stress ratio (Eq. (3))
Q	Energy of band gap
q: q_0	Time-temperature parameter (Eq. (8)): for a test at 295 K
R: R_B, R_c	Resistance per unit length: of boron sheath, of core
T	Temperature, K
t	Time, sec
U	Internal energy
α	Coefficient of thermal expansion
γ : γ_B, γ_c	Resistivity: of boron sheath, of core
ϵ : ϵ^D, ϵ_s	Strain: total deformation strain, surface strain
λ	Thermal expansion strain
ρ : ρ_B, ρ_c	Density: of boron sheath, of core
σ : σ_s, σ^*	Stress: surface stress, transition stress for A
ψ : ψ_L, ψ_H	Damping capacity: at low stress, at high stress
<u>Superscripts:</u>	
a	Anelastic
e	Elastic

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TABLE I. - ELASTIC MODULI AT 295 K FOR BORON (ON W) FIBERS

As-received diameter, μm	Young's modulus, E_Y^e , GN/m^2	Flexural modulus, E_b^e , GN/m^2	Shear modulus, G^e , GN/m^2	Poisson's ratio
102		402 $\pm$ 6	176 $\pm$ 4	0.14 $\pm$ 0.04
203	^a 412 $\pm$ 8 ^b 423 $\pm$ 14	400 $\pm$ 2	177 $\pm$ 4	0.13 $\pm$ 0.03
375		397 $\pm$ 2	179 $\pm$ 2	0.11 $\pm$ 0.02
Average	418 (60.5 $\times$ 10 ⁶ psi)	400 (58.0 $\times$ 10 ⁶ psi)	177 (25.7 $\times$ 10 ⁶ psi)	0.13

^aFrom fiber elongation at 77 K.^bFrom boron/aluminum mechanical resonance.^cFrom fiber mechanical resonance.

TABLE II. - DENSITY OF BORON FIBERS

	As-received				Etched ^a		
Diameter, μm	142.1	202.1	374.1	142.3	194.1	147.3	138.9
Number of fibers (substrate) ^b	3 (W)	3 (W)	3 (W)	1 (C)	1 (W)	1 (W)	1 (W)
Density, ^c g/cm ³	2.4751	2.4099	2.3651	2.2946	2.4162	2.4698	2.4843

^aAs-received diameter of 203 μm .^bTungsten (W) or carbon (C).^cMaximum standard deviation for all data was 0.0003 g/cm³.ORIGINAL PAGE IS
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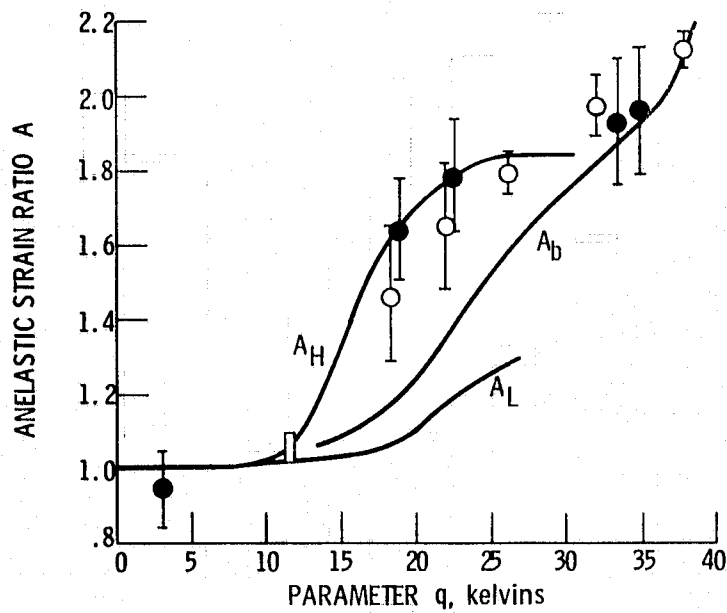


Figure 1. - Time-temperature dependence of the anelastic strain ratio A for boron fibers. A_L was measured at low flexural stresses; A_b at high flexural stresses; and A_H at high axial stresses.

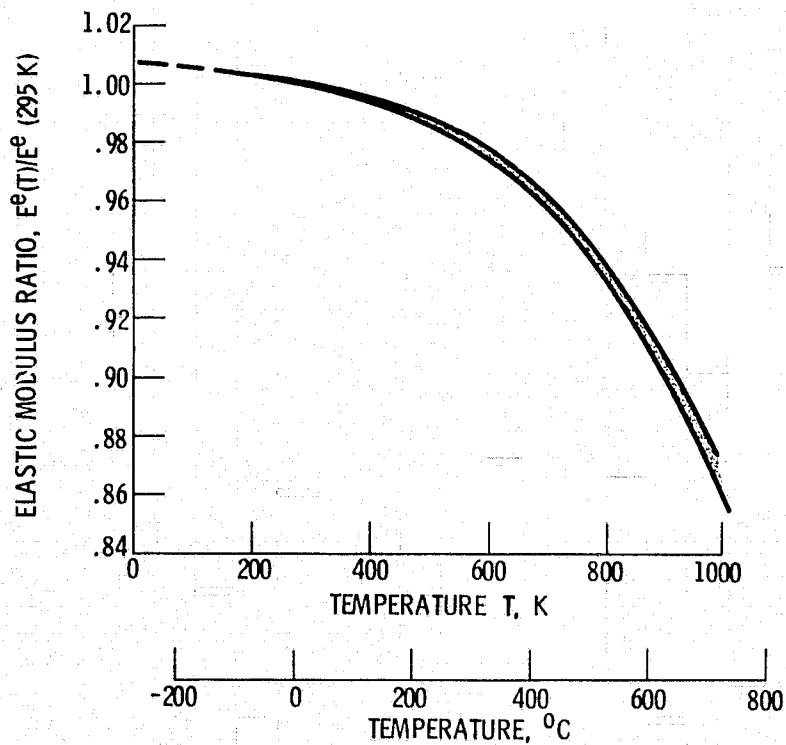


Figure 2. - Temperature dependence of the elastic moduli of boron fibers as derived from flexural resonant frequency data and anelastic theory.

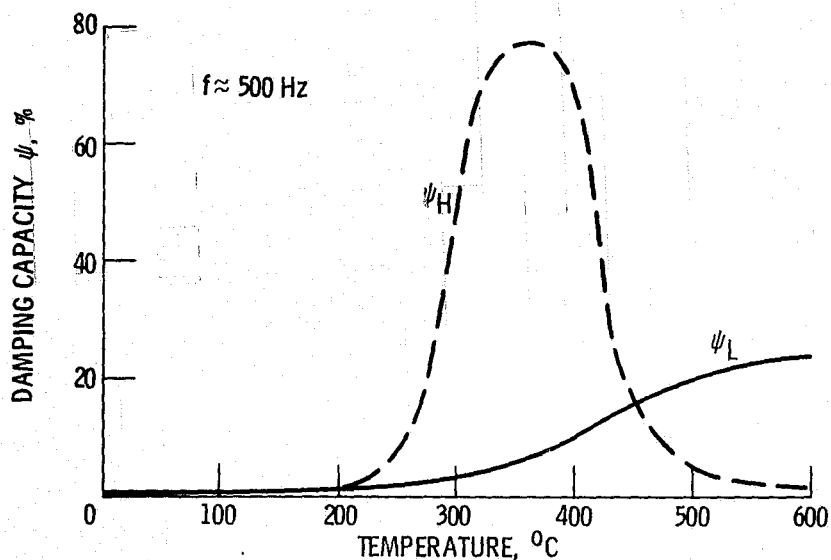


Figure 3. - Temperature dependence of ψ , the damping capacity or relative energy loss per cycle, for boron fibers vibrating near 500 Hz. ψ_L was measured at low stresses; ψ_H was estimated from $A_H(q)$ for high stress axial vibrations.

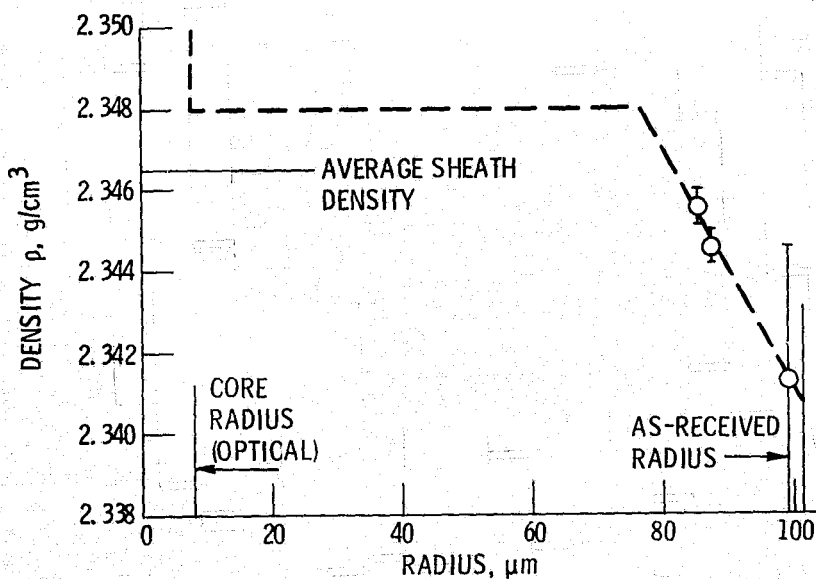


Figure 4. - Estimated radial density distribution within the sheath of as-received 203 μm boron on tungsten fibers.

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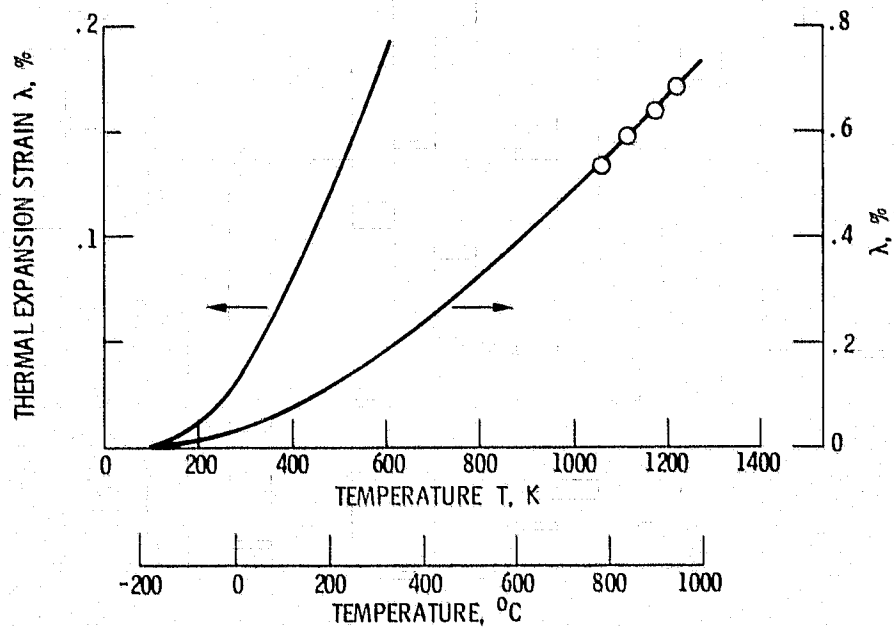


Figure 5. - Temperature dependence of the thermal expansion strain for 203 μm boron on tungsten fibers.

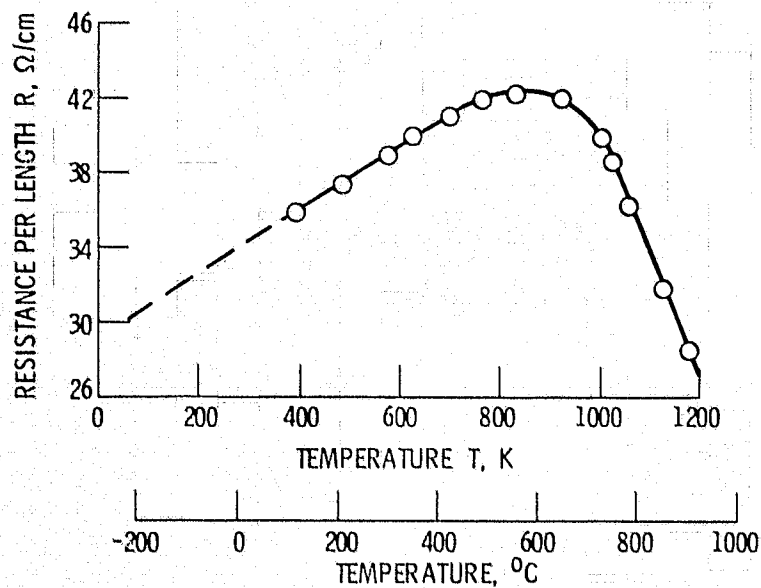


Figure 6. - Temperature dependence of R, the resistance per unit length for 203 μm boron on tungsten fibers.